STRONTIUM ISOTOPE SYSTEMATICS OF COAL UTILIZATION BYPRODUCTS AND THEIR INTERACTIONS WITH ENVIRONMENTAL WATERS

by

Tonya M. Brubaker

B.A., University of Pittsburgh, 2007

Submitted to the Graduate Faculty of

Arts and Sciences in partial fulfillment

of the requirements for the degree of

Master of Science

University of Pittsburgh

2010

UNIVERSITY OF PITTSBURGH

School of Arts and Sciences

This thesis was presented

by

Tonya M. Brubaker

It was defended on

August 10, 2010

and approved by

Daniel J. Bain, Assistant Professor, Department of Geology and Planetary Science, University of Pittsburgh

Rosemary C. Capo, Associate Professor, Department of Geology and Planetary Science, University of Pittsburgh

Thesis Advisor: Brian W. Stewart, Associate Professor, Department of Geology and Planetary Science, University of Pittsburgh

STRONTIUM ISOTOPE SYSTEMATICS OF COAL UTILIZATION BYPRODUCTS AND THEIR INTERACTION WITH ENVIRONMENTAL WATERS

Tonya M. Brubaker, MS

University of Pittsburgh, 2010

The major element and strontium isotope systematics and geochemistry of coal utilization byproducts (CUB) and their interactions with environmental waters were investigated using laboratory leaching experiments with water, sodium carbonate, acetic acid, nitric acid, and hydrochloric acid. Analysis of elemental data from both column and sequential leaching procedures shows rapid release of most major elements early in the leaching procedure, excluding silicon and iron, suggesting association with soluble and surface bound phases. Possible sulfate mineral phases can be inferred due to the high proportions of S leached with sodium carbonate solution, effective at dissolving sulfates such as anhydrite ($CaSO_3$). For all elements except sulfur, highly acidic leachates were most effective in extracting elements from the CUB. In both the column and sequential leaching procedures silicon was leached most effectively by stronger acidic solutions later in the experiment, suggesting the presence of a more resistant silicate phase, possibly residual biotite, feldspar, or clays, or an amorphous glass phase formed during combustion.

Isotopic results from the column leaching experiment show a marked increase in $^{87}Sr/^{86}Sr$ ratio with continued leaching. This general trend is also seen in the sequential leaching data, showing an increase in $^{87}Sr/^{86}Sr$ ratio with continued leaching in increasingly acidic solutions. These data show that there are isotopically distinct phases within the CUB, suggesting the

presence of a more resistant, highly radiogenic phase that survives the combustion process and is leached after the more soluble minerals are removed. The Sr isotope systematics and leaching behavior of the Class F CUB samples demonstrate that isotopic homogenization of minerals in coal does not always occur during the combustion process, despite the high temperatures encountered in the boiler. A key factor in accessing more resistant phases within CUB appears to be the extent of leaching, rather than the particular leaching procedure or acid used. Early-released Sr tends to be isotopically uniform; thus the Sr isotopic composition of CUB could be distinguishable from other sources and a useful tool for quantifying the possible contribution of fly ash leaching to the total dissolved load in natural surface and groundwaters.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1.0 INTRODUCTION

Coal combustion generates more than 50% of the electricity used in the United States and about 40% of that used worldwide (Kim and Hesbach, 2009; Vejahati et al., 2010). The combustion of coal for energy generation results in the production of coal utilization byproducts (CUB) including fly ash, bottom ash, boiler slag, fluidized bed combustion ash and other solid fine particles (Asokan et al., 2005). During the combustion process, fly ash (which comprises ~80% of coal-fired power plant combustion residue; (Dutta et al., 2009)) is transported out of the boiler by exhaust gases, then most of it collected and transported to market or to a landfill (Yeheyis et al., 2008). The amount of fine ash that escapes collection and is then emitted into the atmosphere varies between power plants, ranging from 10% in older installations to 0.5% in modern emission-controlled facilities that use electrostatic precipitators (ESP) or fabric filters (Depoi et al., 2008).

The US, China, and India are the top producers of coal combustion residues, producing more than 300 billion kg/year; this is a strong driver for finding value-added products using this material (Asokan et al., 2005). Coal utilization byproducts are currently used in bricks, cement, concrete, wallboard, mining materials, adhesives, paint, and as a soil amendment and wood substitute (Feeley et al., 2004; Yeheyis et al., 2008). CUB has also been used as a coal mine grouting material that takes advantage of the alkalinity-generating capacity of fly ash to neutralize acid mine drainage (AMD) (Dutta et al., 2009; Hamel et al., 2010). Production of one

ton of fly ash in concrete reduces CO_2 emissions by two tons, and has a higher resistance to lime leaching and water penetration than standard Portland cement. Use of CUB in construction projects surrounding power plants is mandatory in India. A study by the American Coal Ash Association (ACAA, 2004) estimates that of the 122 million tons of CUB produced annually in the US (as of 2003), approximately 46 million tons are marketed for beneficial use.

In areas such as the northeastern US, environmental effects of fly ash disposal, as well as combined sewage overflow, coal mine drainage, and natural gas extraction can potentially affect both drinking water aquifers and surface water ecosystems. The isotopic composition of impacted waters could offer information about the source(s) of contamination, the migration pathways and aid in the development of appropriate remediation strategies.

This study documents the geochemical and strontium isotopic composition of leachates extracted from four different Class F fly ashes using both column and batch leaching methods. Samples were treated with different solutions simulating varying environmental conditions such as acid rain, AMD, and long-term alkaline conditions found in typical impoundments. Leachates were analyzed for elemental composition as well as Sr isotopic composition.

2.0 BACKGROUND

2.1 MINERALOGY OF COAL UTILIZATION BYPRODUCTS

The utilization and disposal of CUB materials and their possible environmental effects require a more detailed assessment of their mineralogical and chemical properties. The formation of CUB materials from coal-burning power plants is directly influenced by many factors, including the mineralogical and chemical composition of the feed coal, the processes involved with preparation and burning of the coal, and the removal and storage of the waste materials (Vassilev and Vassileva, 1996; Kutchko and Kim, 2006).

Fly ash is a heterogeneous material represented by particles smaller than 100 μm in size composed of inorganic and organic components. The organic constituents consist of residual coal particles, while the inorganic fraction of CUB materials comprises both crystalline and amorphous phases (Vassilev and Vassileva, 1996). Coal-burning furnaces typically operate at temperatures in excess of 1400° C, where minerals can decompose through oxidation or other reactions, disintegrate and/or agglomerate, and partially to completely melt (Kutchko and Kim, 2006). Rapid cooling after combustion can result in the formation of amorphous, spherical particles. The resulting inorganic spherical particles are the product of melting, partial melting, or vitrification of coal minerals such as quartz, mica, clay minerals and other mineral combinations with relatively low melting points (Vassilev and Vassileva, 1996; Vejahati et al.,

2010). Hollow spheres may be filled with gas formed during combustion as a result of decomposition of organics, carbonates, and sulfates, as well as evaporation of pore water (Kim and Kazonich, 2004).

The crystalline component of the inorganic fraction of CUB is composed of various major, minor, and accessory mineral phases. The origins of these phases can be primary – minerals originating in coal that have undergone no phase transitions; secondary – phases formed during combustion; or tertiary – phases formed during the transport and storage of CUB materials (Vassilev and Vassileva, 1996). Table 1 shows some of the common minerals that can be found in CUB, as identified by Vassilev and Vassileva (1996). In Class F fly ashes, the main silicate minerals include quartz, mullite, clays, and feldspars while oxides and sulfates are the major non-silicate minerals (Kim and Kazonich, 2004).

Silicate phases within CUB are mainly primary minerals and secondary products, with quartz being the most prevalent. Secondary quartz forms at temperatures greater than 900°C from silica liberated during the phase transformations of clay minerals, mica, and feldspars (Martinez-Tarazona, 1996; Vassilev and Vassileva, 1996). Cristobalite and mullite are also found in CUB, forming from the decomposition, transformation and recrystallization of clay minerals and other silicate minerals. Feldspars form as a result of solid phase reactions between aluminosilicates and liberated Ca, K, and Na oxides. While kaolinite tends to be a primary mineral, metakaolinite (a dehydrated kaolinite phase) represents thermally altered clay minerals (Vassilev and Vassileva, 1996). Micaceous minerals are mainly primary in occurrence and are typically muscovite.

Magnetite, hematite, and other oxides have also been found in CUB, originating mainly from the oxidation of pyrite and other iron oxides and the crystallization of iron rich mineral

melts. Ca and Mg oxyhydroxides are usually formed during CUB storage as lime and periclase are hydrated, forming more stable phases such as portlandite and brucite (Vassilev and Vassileva, 1996). Sulfates are generally secondary or tertiary in occurrence, the most prevalent being gypsum and anhydrite.

Trace elements such as mercury, arsenic, selenium, lead, and strontium are present in CUB and are classified as public health concerns. These elements are typically volatilized during combustion and then condense onto previously existing fine ash particles. Retention of these potentially harmful elements is heavily influenced by mineral associations (Vejahati 2010).

Table 1 Major and minor phases in CUB. Compiled from Vassilev and Vassileva (1996), Table 3

Major to minor phase[a]		Minor to accessory phase[a]	
Silicates			
Quartz	SiO_2	Cristobalite	SiO_2
Kaolinite	$Al_2Si_2O_5(OH)_4$	Wollastonite	$CaSiO_3$
Mullite	$Al_6Si_3O_{15}$	Melilite	$(Ca,Na)_2(Al,Mg,Fe)(Si,Al)_2O_7$
Plagioclase feldspar	$Na_xCa_{(1-x)}Al_{(2-x)}Si_{(2+x)}O_8$	Monticellite	$CaMgSiO_4$
K-feldspar	$KAlSi_3O_8$	Olivine	$(Mg,Fe)_2SiO_4$
		Pyroxene	$(Ca,Na)(Mg,Fe,Al)(Si,Al)_2O_6$
		Chlorite	$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2$
		Mica	$KAl_2(AlSi_3O_{10})(OH)_2$ - $K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$
		Rankinite	$Ca_3Si_2O_7$
		Larnite	Ca_2SiO_4
Oxides and Hydroxides			
Hematite	Fe_2O_3	Lime	CaO
Magnetite	Fe_3O_4	Portlandite	$Ca(OH)_2$
		Maghemite	γ-Fe_2O_3
		Limonite	$FeO(OH)\cdot nH_2O$
		Magnesioferrite	$MgFe_2O_4$
		Spinel	$MgAl_2O_4$
		Periclase	MgO
		Brucite	$Mg(OH)_2$
		Corundum	Al_2O_3
		Al hydroxides	$Al(OH)_3$
Sulfates			
Gypsum	$CaSO_4 \bullet 2H_2O$	Fe sulfates	$FeSO_4$
Anhydrite	$CaSO_4$	Mg sulfates	$MgSO_4$
		Alunite	$KAl_3(SO_4)_2(OH)_6$
		Barite	$BaSO_4$
Carbonates			
		Calcite	$CaCO_3$
		Dolomite	$CaMg(CO_3)_2$
Non-crystalline phases			
Glass Organic matter			

[a]Major phase: >1 wt.%; minor phase: 0.1-1 wt.%; accessory phase: <0.1 wt.%.

2.2 TRACE ELEMENTS IN COAL UTILIZATION BYPRODUCTS

The elements found in coal can be divided into three general classifications based on concentration – major elements, with concentrations above 1000 ppm; minor elements, with concentrations between 100 and 1000 ppm; and trace elements, with concentrations below 100 ppm (Vejahati et al., 2010). Trace elements, including some hazardous to human health, tend to be enriched in the finest CUB materials, which have a long atmospheric residence time, can be inhaled deep into the human respiratory system, and are likely to be leached during interactions with environmental waters (Martinez-Tarazona, 1996).

Trace elements are also categorized according to how they are partitioned between the different types of CUB. Group I elements (Ba, Ce,Cs, Mg, Mn) tend to be concentrated equally between coarse slag and fine particles. Group II elements (As, Cd, Pb, Se, Zn) are traditionally more concentrated in finer particulates, which have potential to escape particulate control systems. Group III elements are volatilized during the combustion process and are concentrated in the gas phase (Martinez-Tarazona, 1996; Vejahati et al., 2010). CUB, including fly ash, can contain significant quantities of potentially leachable toxic elements such as arsenic (As; 0.5 -80 ppm), mercury (Hg; 20-1000 ppb), and selenium (Se; 0.2 -4ppm) (Xu et al., 2004), as well as other trace elements of environmental concern such as boron (B), chromium (Cr), lead (Pb), nickel (Ni), strontium (Sr), vanadium (V) and zinc (Zn) (Querol et al., 1995). Although the majority (~89%) of mercury is released to the environment primarily as vapor in stack emissions (Bignoli, 1989), >90% of most elements present in coal are not released in stack gases (Vejahati et al., 2010). High concentrations of toxic heavy metals can limit use of fly ash as a zeolitic sorbent material or its use in ceramics or as mine grout. Harmful trace elements have the

potential to leach from CUB materials into environmental fluids such as acid rain, groundwater, and acid mine drainage.

CUB has been used as a soil amendment and in land reclamation. Although in one study cabbage yields were higher and nutritional content and heavy metal concentrations were within quality standards (Asokan et al., 2005), other studies associate agricultural use of CUB with heavy metal toxicity, phosphorous deficiency, and salinization (Shukla and Mishra, 1986). While the percentage of collected CUB used in recycled products is steadily increasing, the majority is still disposed of in landfills or settling lagoons where it has the potential to interact with environmental fluids such as precipitation, runoff and groundwater (Yeheyis et al., 2008; Bhattacharyya et al., 2009). The 2008 impoundment failure at TVA's Kingston Fossil Plant in Tennessee illustrates both the potential hazards of long-term fly ash storage and the need for tests that can assess both the extraction potential of environmentally significant chemical species and their pattern of release over long time periods (Kim and Hesbach, 2009; Ruhl et al., 2009). Many studies focus on elements of concern for drinking water quality, which are primarily associated with the inorganic iron sulfides present in coal (e.g., As, Cd, Hg, Mo, Se, Sb). However, fly ash in contact with water can also potentially release significant quantities of elements associated with silicate mineral matter in coal such as aluminum, calcium, sodium, chromium, and vanadium, which can have toxic effects on plants and aquatic organisms, as well as result in high total dissolved solid (TDS) inflows to streams, lakes and wetlands.

Better knowledge of the factors such as coal mineral matter content, power plant conditions (e.g., wet vs. dry scrubbing; (Vejahati et al., 2010), and environmental conditions that govern release of volatile toxic elements such as As, Hg, and Se are required to optimize safe use of CUB and to develop appropriate long-term storage solutions. It is important to determine the

extent to which CUB minerals and phases retain and release potentially toxic metals while interacting with environmental waters under variable pH and redox conditions.

2.3 CUB AND LEACHING EXPERIMENTS

Leaching experiments have been performed to determine the extent to which different trace elements are leached from CUB into environmental fluids. Recent reviews suggest that while quantitative predictions of element retention and mobility under actual natural conditions is challenging, the development of rapid, reproducible standardized tests is key to understanding the association of coal mineral matter and environmental conditions with toxic element release, and adopting appropriate standards for CUB to govern safe use (Hassett et al., 2005; Vejahati et al., 2010). Current procedures include serial batch leaching (Kim and Hesbach, 2009), synthetic groundwater leaching (SGLP (Hassett, 1998)) mine water leaching (Ziemkiewicz et al., 2003) as well as the EPA-developed toxicity characteristic leaching procedure (TCLP; USEPA Method 1311). Kim and Hesbach (2009) conducted a comparison of five leaching techniques and found that cumulative elemental release by weight of sample was lower for the procedures conducted under alkaline (SGLP) to mildly acidic (TCLP) conditions. Fly ash in contact with natural waters generally produces high-pH conditions that affect the mobility of elements such as As, Mo and V, whereas contact with low-pH fluids tend to mobilize metals such as Cu, Ni, Pb and Zn (Kim and Hesbach, 2009). Hassett et al. (2005) also note differences in empirically determined element mobility based on batch and column leaching studies, and emphasized the role of formation of secondary minerals such as ettringite (hydrated Ca-Al-sulfate hydroxide) in the retention of elements present as oxyanions (e.g., B, As, Cr, Mo, Se and V).

Numerous studies have been conducted that examine the solubility and leaching potential of CUB (Querol et al., 1996; Sheps-Pelleg and Cohen, 1999; Querol et al., 2001; Hassett et al., 2005), including assessing the leaching characteristics of CUB products used for primary and secondary materials in construction (Querol et al., 2001) and for grouting mines (Hamel et al., 2010). Coal utilization byproducts are potentially useful in ameliorating the effects of acid mine drainage (AMD), and alkaline fly and bottom ashes are used to grout abandoned mines and neutralize acidic discharges from these sites. However, studies have also demonstrated the mobility of certain trace metals in CUB, clearly warranting further research into the interaction between CUB and the aqueous environment (Hamel et al., 2010).

Sequential leaching procedures, in combination with strontium isotope analysis, have also been performed on CUB materials to help elucidate the various mineral reservoirs within CUB and possible elemental associations (Spivak-Birndorf, 2007). Samples were sequentially leached with water, HOAc, and HCl, respectively, to target elements associated with specific phases in CUB including water soluble phases (sulfates and some carbonate), dilute HOAc soluble phases (carbonates), and HCl soluble phases (phosphates and possible aluminosilicates). Strontium isotope analysis was also performed on the sequential leaching solutions.

This sequential leaching study found that potentially harmful elements were leached from CUB in water (B, Cr, Mo, Se, F) and acetic acid (Zn, Cu, Mn, Cr, Ni, Co, Sb, Cd), while others (Pb, V, As) were soluble in HCl (Spivak-Birndorf, 2007). Elements mobilized during the water-leaching step of the sequential leaching procedure are presumed to be associated with sulfate minerals, with anhydrite being the dominant phase (Kim, 2003; Spivak-Birndorf, 2007). Additionally, significant variations in $^{87}Sr/^{86}Sr$ ratios were found between the leachate and whole CUB samples, indicating the presence of isotopically distinct Sr-bearing phases. This suggests

that the mineral phases in coal remain isotopically heterogeneous, despite the high temperatures encountered in the boiler during the combustion process.

Column leaching experiments have been conducted to determine the distribution of metals between the silicate and non-silicate fractions in CUB and their release patterns (Kim and Kazonich, 2004). Several Class F CUB samples were treated following a procedure nearly identical to that outlined in this study, with the exception of the use of sulfuric acid rather than nitric. Researchers found that different elements had differing associations between the silicate and non-silicate fraction. Of the trace elements studied; Be, Cd, and Pb were associated with the silicate phase, while As and Se were predominately associated with non-silicates. Elements associated with the non-silicate phases were more soluble in alkaline solutions, while those associated with the silicate fraction were more soluble in acidic solutions. The solubility of most elements in the CUB was relatively low, but the distribution of metals among phases does influence the release pattern, and therefore warrants further study.

2.4 STRONTIUM ISOTOPE SYSTEMATICS AND CUB

Natural isotope compositions of fluids that have interacted with various solids have been long used to identify the source of chemical species in natural and human-impacted waters and to track fluid flow. Strontium (Sr) isotopes are well established as tracers in geologic and environmental systems, including water-rock interactions (Capo et al., 1998; Banner, 2004; Hamel et al., 2010). Strontium isotope ratios (expressed as $^{87}Sr/^{86}Sr$) can be used to identify different phases within the CUB that may carry potentially toxic trace metals, as well as to provide insight into the behavior of other elements in CUB as they interact with environmental

waters. Trace element partitioning studies of coal combustion indicate that strontium is among the group of elements (including Ba, Be, Co, Cr, Mo, Pb, Zn) that condense within the coal-fired power plant vs. those such as mercury and selenium that are volatilized (Vejahati et al., 2010).

Previous studies regarding strontium (Sr) isotopes and CUB focus primarily on using this isotope system as an environmental tracer (Hurst and Davis, 1981; Straughan et al., 1981; Hamel et al., 2010). Strontium has four naturally occurring stable isotopes: ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr. Of these, only the relative abundance of ^{87}Sr varies significantly in natural systems due to the radioactive decay of ^{87}Rb. Rubidium has two naturally occurring isotopes, ^{85}Rb and ^{87}Rb, of which ^{87}Rb undergoes radioactive ß$^-$ decay to stable ^{87}Sr, with a half-life of ~48.8 x 10^9 years. The ^{87}Sr concentration in geologic materials will increase over long time scales as a result of the beta decay of ^{87}Rb. Different geologic materials to vary in their Sr isotopic ratios, commonly expressed as $^{87}Sr/^{86}Sr$, due to differences in age and long-term Rb/Sr ratios. These variations can be used to identify the sources of the strontium to aqueous geological and environmental systems. These sources can include mineral matter associated with the feed coal and/or thermally altered and newly precipitated minerals inheriting the Sr isotopic composition(s) of their precursors.

Strontium in CUB is enriched relative to coal and a significant fraction is readily available for mobilization (Hurst et al., 1991). Variations in strontium isotope composition can potentially be used to distinguish between the various phases within CUB, both detrital and neoformed, that contain trace metals whose mobility would be affected by their phase associations. Strontium isotopes can also be used to determine the extent to which other trace elements, especially those with affinities to Sr, are affected during combustion and how they are mobilized when interacting with environmental waters. Spivak-Birndorf (2007) found that CUB

can preserve the isotopic composition of primary mineral matter found in coal and retain significant isotopic heterogeneity during combustion, despite core burning temperatures as high as 1800°C (Mackowsky, 1982).

3.0 EXPERIMENTAL METHODS

3.1 COLUMN LEACHING EXPERIMENTAL DESIGN

Four different samples of Class F coal utilization by-product (CUB) were put through a column leaching procedure at the National Energy Technology Laboratory (NETL) in Pittsburgh, Pennsylvania. Class F fly ash is produced from the combustion of bituminous and anthracite coal, commonly used in pulverized coal power plants in Pennsylvania and West Virginia. They are defined as containing a minimum 70 wt % concentration of major oxides, in contrast to Class C ashes, which are derived from lower grade (but often sub-bituminous) coal and lignite (Feeley et al., 2004). Minerals identified in Class F ashes similar to those in this study include quartz, mullite, calcite, magnetite and hematite (Vassilev and Vassileva, 1996; Karayigit and Gayer, 2001; Spivak-Birndorf, 2007).

Each CUB sample was split into three 1 kg aliquots, which were placed in individual up-flow PVC columns. Columns were constructed of 30 cm long sections of 5 cm inner diameter clear PVC pipe, which were capped and drilled to accommodate 6.4 mm compression fittings to control leachant inflow and outflow (Figure 1). The end caps were filled with plastic beads, contained by a fine-mesh screen, to minimize dead volume and back mixing. Leachants were pumped through the vertical columns via an Ismatec Model 78001-10 peristaltic pump at a rate of 0.2 ml/min.

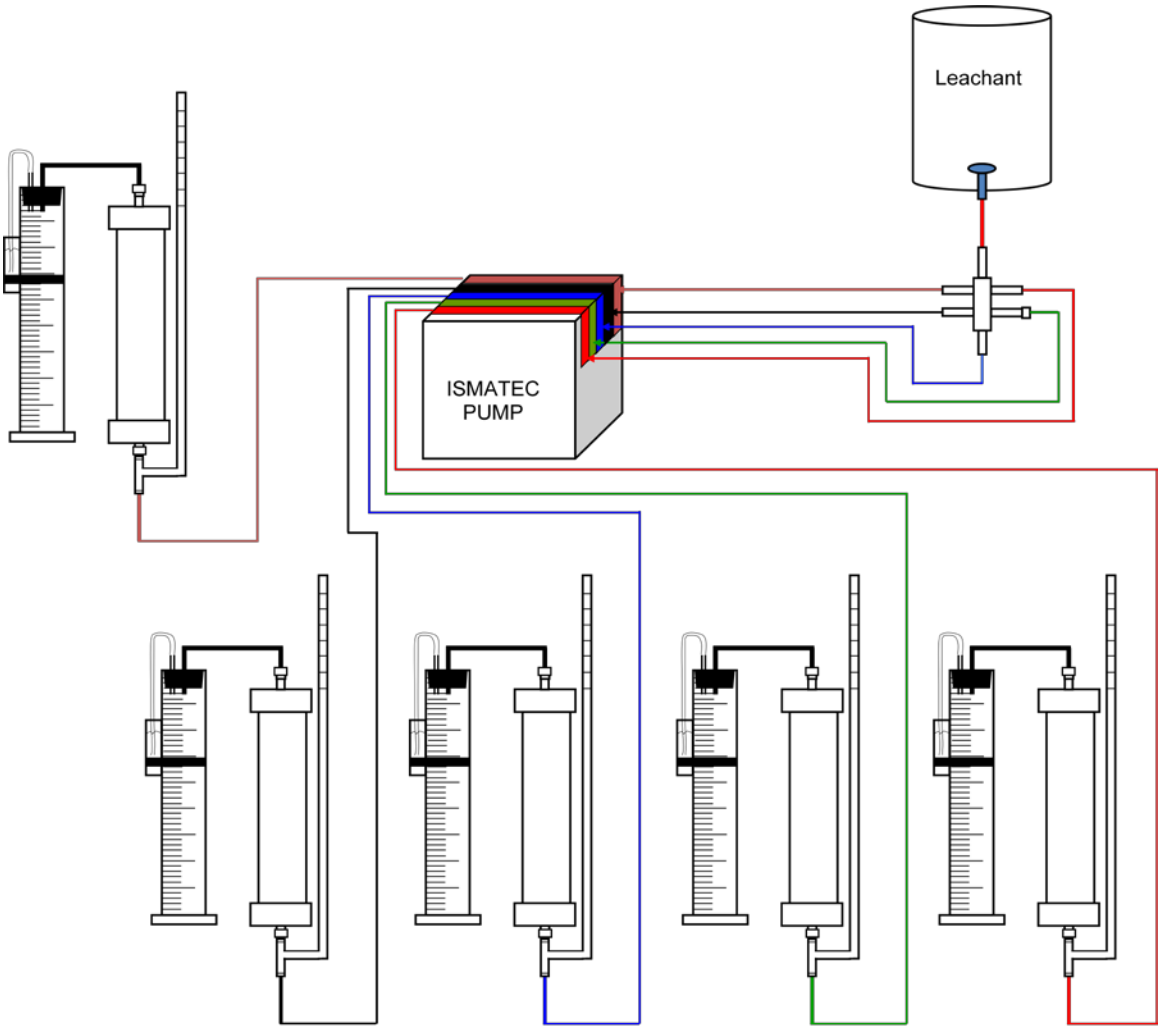

Figure 1 Experimental design of CUB leaching columns. Provided by K. Schroeder, NETL

The columns were pumped with solutions of nitric acid, acetic acid, and sodium carbonate to represent a range of pH values and simulate different environmental fluids. Acetic acid (pH 2.9), a weak organic acid, has been used in other studies as a proxy for potential leaching during co-disposal in a municipal solid waste landfill (Kim and Kazonich, 2004). Sodium carbonate (pH 11.1) was used to investigate behavior of elements that are mobilized under high pH conditions. Numerous studies (e.g., Hassett et al. (Hassett et al., 2005) and references therein) indicate that fly ash in contact with natural waters generate alkaline solutions that are associated with mobility of elements that form oxyanions (e.g., As, Se, Sb) and the precipitation of secondary hydrated minerals such as ettringite (a hydrated calcium aluminum sulfate hydroxide). Nitric acid (pH 1.0) was used to mimic the extremely low pH of acid mine drainage that would be in contact with CUB that is used to grout abandoned mines. Although oxidation of pyrite in coal mine spoil produces sulfuric acid, nitric acid was used to avoid the possible clogging of columns with insoluble sulfates that occurred in earlier studies (Kim, 2003).

Several ten-liter batches of leachant solution were prepared at NETL over the duration of the experiments. Sodium carbonate was prepared by adding 53g of Na_2CO_3 (anhydrous) to 10 liters of Millipore Q water (MQW). Acetic acid was prepared by adding 57 mL of glacial acetic acid to 10 liters MQW. Nitric acid was prepared by adding enough concentrated HNO_3 to MQW to achieve a pH of 1.

Samples were leached at ambient temperature for a period of 100 days, excluding sample FA41 in the nitric acid experiment, which clogged during the first week. Leachate samples of approximately 30-40 mL were collected from each column every 2-3 days, and pH was measured before instrumental analysis. Aliquots were taken for elemental and isotopic analysis. Samples were preserved with ultrapure nitric acid and refrigerated prior to elemental analysis.

3.2 BATCH LEACHING EXPERIMENTAL DESIGN

Batch leaching procedures were performed at the University of Pittsburgh on three samples of CUB that were also analyzed by column leaching procedures (FA24, FA38, FA49). Samples of CUB were split to produce a sample size of ~0.5 g. Each CUB sample was placed in an acid-cleaned 50 mL centrifuge tube, including two 0.5 g splits of FA24 for replicate analysis. A total liquid-to-solid ratio (LTS) of 100:1 was used. Hassett et al. (2005) reported that a LTS of 20:1 was commonly used in the past to allow for analytical determination of trace elements, but that LTS was not necessarily a critical factor for trace elements in fly ash leachates. Kim and Hesbach (Kim and Hesbach, 2009) compared five fly ash leaching methods in which a wide range of LTS were used and found general agreement between methods.

First, 50 mL of Milli-Q water was added to each sample, which was then shaken for a period of eight hours at ambient temperatures. The samples were centrifuged, and the supernatant collected in an individual 60 mL HDPE bottles cleaned in 30% nitric at 80°C and rinsed in MQW water. Next, 50 mL of 0.1N acetic acid (HOAc) was added to the same centrifuge tube and shaken for a period of two hours. The samples were then centrifuged, and the supernatant collected in an individual acid-cleaned 50mL HDPE bottle. Lastly, 50 mL of 1N hydrochloric acid (HCl) was added to the same centrifuge tubes and shaken for a period of 2 hours. The samples were then centrifuged, and the supernatant collected.

3.3 ANALYTICAL PROCEDURES

Elemental concentrations of the CUB column leachates were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS) at NETL. Elemental concentrations of the CUB batch leachates were determined by ICP-OES at the University of Pittsburgh.

For strontium isotope analysis, aliquots of the leachate solutions containing ~2 μg of strontium (if available) were evaporated to dryness in acid-washed Teflon vials on a 100°C hotplate under a HEPA-filtered hood. Samples were re-dissolved in HNO_3, and passed through quartz glass or Teflon® columns filled with Eichrom® Sr Resin. Each sample was eluted with nitric acid to remove all elements except Sr. Strontium was then eluted with water and collected in a Teflon® beaker. Samples were then evaporated to dryness under HEPA filtration for isotopic analysis.

Approximately 500 ng of Sr were loaded onto single Re filaments with a tantalum oxide activator solution. The Sr isotopic compositions were measured on a Finnigan MAT 262 multicollector thermal ionization mass spectrometer (TIMS) at the University of Pittsburgh. A total of 100 ratios were measured during each analysis, with instrumental mass fractionation corrected using $^{86}Sr/^{88}Sr = 0.1194$. Interference from ^{87}Rb was monitored by measuring ^{85}Rb on a separate detector. The mean $^{87}Sr/^{86}Sr$ value for strontium isotope standard SRM 987 over the period of these analyses was 0.71024.

4.0 RESULTS

4.1 COLUMN LEACHING EXPERIMENTS – ELEMENTAL DATA

Concentrations of selected major elements (Al, Ca, Fe, Mg, Na, S, Si) in CUB samples from the column leaching experiments are presented in Table 2 and shown in Figure 2. Of the three leachants used, nitric acid generally extracted the greatest amount of major cations (Al, Ca, Fe, K, Mg, Na, Si), while S was extracted by all three leachates at approximately equal levels.

Most elements showed a trend of maximum concentrations at or near the beginning of the leaching experiment, followed by a general tapering off (Fig. 2). Major exceptions to this trend are Al, Fe, Mg and Si, which in most samples display a trend of low initial values followed by a spike in concentration, and steady, relatively high concentrations thereafter. Elemental data for sample FA41 nitric acid leach are unavailable for the last two sampling volumes, as the column became clogged during the first week of the experiment.

Of the three leachates used in the column experiments, the four fly ash samples displayed the most coherent leaching behavior over time with sodium carbonate (Fig. 2). The behavior of samples with the acid leaching solutions tended to be variable, especially in the early stages of leaching (up to 5 L cumulative volume). This could reflect the varying acid neutralization capacities of the different fly ash samples – once the acid was neutralized, then most elements were leached at a relatively constant rate.

Table 2 Selected elemental concentrations of CUB column leachates in mg/L. Vol (L) represents cumulative volume through the columns at the time of collection.

					Sodium Carbonate					
FA24	**Vol. (L)**	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Na**	**S**	**Si**	**Sr**
	0.26	0.43	404.00	<DL	18.95	148.46	sat'd	904.00	9.75	0.17
	0.80	18.20	4.64	0.02	10.29	0.22	sat'd	27.90	2.87	0.01
	1.16	20.59	2.11	<DL	13.50	0.24	sat'd	22.10	2.59	0.02
	10.72	9.24	0.76	0.04	3.49	0.14	sat'd	4.13	8.74	0.00
	21.93	6.99	0.76	0.02	2.01	0.19	sat'd	2.23	10.41	<DL
FA38	0.20	0.17	718.00	<DL	337.92	0.58	sat'd	1,400.00	2.31	42.64
	0.78	0.20	643.00	<DL	28.45	<DL	sat'd	1,058.00	2.52	16.46
	1.63	<DL	546.00	<DL	10.93	<DL	sat'd	1,061.00	1.71	7.99
	11.67	10.56	2.17	0.05	0.98	0.39	sat'd	16.80	22.02	0.01
	22.94	2.74	6.78	<DL	1.42	1.56	sat'd	2.54	6.73	0.03
FA41	0.11	399.98	18.40	0.02	184.53	<DL	sat'd	817.00	1.46	6.36
	0.91	339.88	22.20	0.07	9.29	<DL	sat'd	48.90	4.65	2.51
	1.72	205.92	19.00	0.03	3.65	<DL	sat'd	45.40	9.35	1.22
	11.59	70.30	2.48	0.05	1.07	<DL	sat'd	20.60	19.39	0.07
	22.59	75.14	0.57	0.02	1.93	<DL	sat'd	26.70	15.17	0.01
FA49	0.25	43.40	555.00	<DL	99.15	0.27	sat'd	1,211.00	0.65	8.67
	0.83	15.48	23.10	<DL	24.91	<DL	sat'd	586.00	17.31	1.42
	1.69	16.68	2.11	<DL	4.42	<DL	sat'd	58.20	20.59	0.02
	11.70	4.91	1.70	0.02	1.00	1.47	sat'd	3.73	12.38	0.01
	23.03	1.81	2.44	0.00	1.75	1.84	sat'd	3.34	7.46	0.00
					Acetic Acid					
	Vol. (L)	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Na**	**S**	**Si**	**Sr**
FA24	0.23	70.46	847.00	0.27	17.01	158.49	133.75	559.00	108.51	1.47
	0.61	92.71	212.00	0.76	18.30	18.77	7.68	105.00	79.27	2.17
	1.31	67.62	344.00	0.56	8.85	9.74	4.11	<DL	49.25	2.07
	9.84	50.38	802.00	3.02	6.25	4.33	0.91	0.62	39.72	0.84
	19.35	38.05	355.00	1.22	5.68	2.40	0.53	1.72	47.45	0.42
FA38	0.21	0.10	2,290.00	<DL	180.45	0.04	643.12	545.00	0.89	80.15
	0.59	0.13	2,173.00	<DL	36.19	0.04	44.51	331.00	0.97	28.42
	1.33	<DL	1,363.00	<DL	23.07	0.01	18.73	282.00	1.76	19.07
	10.815	114.60	75.60	2.72	2.88	23.95	2.01	2.89	85.10	3.32
	20.985	63.10	28.50	0.78	2.17	8.64	1.29	2.33	82.63	1.66
FA41	0.23	79.04	1,053.00	<DL	96.10	0.06	380.45	1.78	0.93	145.30
	0.635	40.13	1,434.00	<DL	12.47	0.03	23.83	0.67	0.24	112.70
	1.15	<DL	1,398.00	<DL	16.81	92.76	15.18	379.00	0.56	10.98
	11.1	60.98	366.00	6.52	2.62	61.86	5.22	4.72	44.21	9.00
	22.29	32.14	200.00	2.22	1.85	23.38	3.57	2.56	33.65	4.75
FA49	0.2	7.95	1,864.00	<DL	87.68	0.51	303.16	419.00	1.82	35.47
	0.72	0.23	1,997.00	<DL	34.24	0.14	25.85	356.00	3.10	18.33
	1.53	15.60	962.00	0.01	5.68	<DL	13.22	<DL	<DL	61.30
	11.53	61.07	50.00	9.59	2.03	8.31	1.20	0.78	74.34	1.24
	22.6	24.51	16.50	3.78	1.07	2.69	0.36	1.50	50.84	0.51
					Nitric Acid					
	Vol. (L)	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Na**	**S**	**Si**	**Sr**
FA24	0.10	171.11	1,338.00	1.46	21.97	464.06	328.50	783.00	76.49	3.27
	0.77	891.04	307.00	43.62	103.57	91.64	14.21	67.50	279.73	19.77
	1.44	372.64	71.40	63.83	85.53	33.64	9.97	18.80	106.57	7.93
	11.07	387.70	17.10	67.13	58.02	16.55	6.69	6.24	79.83	2.56
	21.22	394.37	14.10	62.16	53.62	15.77	6.15	0.97	111.28	1.89
FA38	0.16	<DL	2,283.00	<DL	373.43	0.05		1,138.00	1.30	90.58
	0.69	<DL	2,902.00	<DL	44.22	0.03	44.26	305.00	1.12	33.22
	1.38	0.08	1,270.00	<DL	28.93	<DL	20.70	119.00	0.43	16.96
	11.40	945.46	252.00	244.44	45.02	58.37	26.01	38.90	251.35	13.59
	22.67	273.53	49.60	104.30	29.91	12.13	16.38	3.70	102.50	3.80
FA41	0.13	11.61	662.00	<DL	143.29	0.04	688.30	191.00	0.21	87.52
	0.64	46.40	1,314.00	<DL	29.81	0.05	55.20	2.40	0.41	160.10
	0.79	5.84	838.00	<DL	13.23	<DL	25.74	<DL	<DL	61.61
	CL	CL	CL	CL	CL	CL	CL	CL	CL	CL
	CL	CL	CL	CL	CL	CL	CL	CL	CL	CL
FA49	0.14	3.08	2,214.00	<DL	90.72	4.42	318.56	315.00	0.55	36.85
	0.76	<DL	2,778.00	<DL	46.77	35.58	38.60	374.00	1.00	24.23
	1.46	<DL	2,066.00	10.76	24.82	250.61	21.76	407.00	5.24	17.88
	11.71	74.78	25.30	97.64	10.03	5.78	3.29	5.04	76.38	1.48
	23.31	36.91	10.20	41.50	5.78	2.80	1.56	1.31	69.61	0.66

CL - Column clogged mid-way through experiment
sat'd - Analysis not complete as column became saturated with element

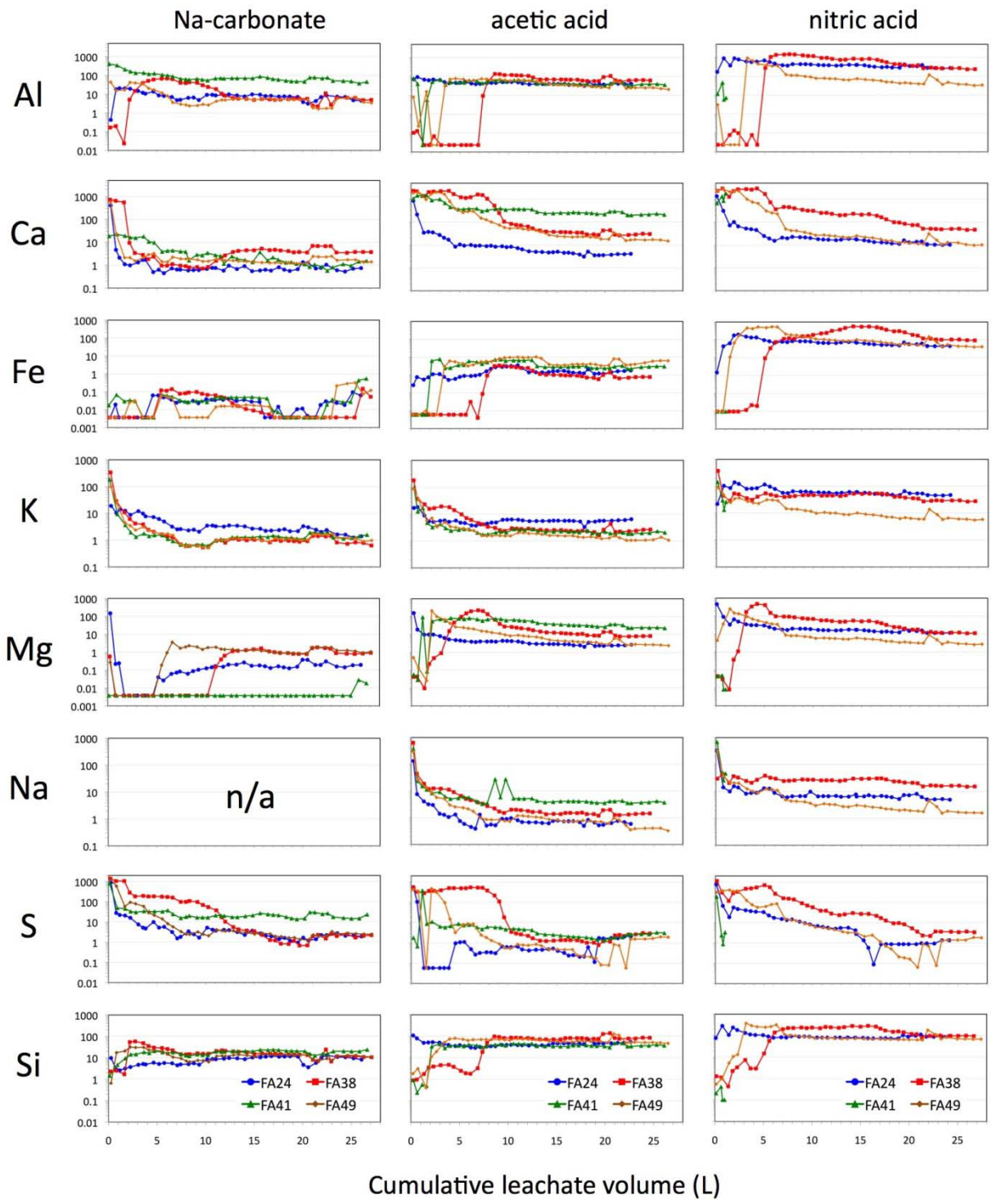

Figure 2 Selected element concentrations (in mg/L) as a function of cumulative leachate volume.

4.2 COLUMN LEACHING EXPERIMENTS – SR ISOTOPIC DATA

The $^{87}Sr/^{86}Sr$ ratios of the column leaching solutions at five different sampling dates (volume of leachant passed through each column on given date given in L) are shown in Table 3. Isotopic ratios were obtained for 58 leachates; high Sr blanks in the leaching experimental columns precluded analysis of ten sodium carbonate leaches, and no nitric acid leachate was obtained for FA41 the last two sampling dates of the experiment due to clogging of the leaching column.

Strontium isotopic ratios are plotted in Figure 3 as a function of cumulative volume of leachant passed through the column. In general, the $^{87}Sr/^{86}Sr$ ratio increased as the experiment progressed. Fly ash FA24 had the greatest increase in $^{87}Sr/^{86}Sr$ ratio, particularly in the nitric acid leach, jumping from 0.711005±12 at the beginning of the experiment to 0.713758±08 at the conclusion of the experiment. Fly ash FA38 showed similar, but less pronounced, increases in $^{87}Sr/^{86}Sr$ ratio, with the nitric acid leach increasing from 0.710770±08 at the beginning of the experiment to 0.711433±09 at the conclusion of the experiment. A slight increase was observed in the $^{87}Sr/^{86}Sr$ ratio for the acetic acid leachates, and the three sodium carbonate samples analyzed were all very close in their $^{87}Sr/^{86}Sr$ ratios.

One observation is that the samples are not isotopically homogeneous despite experiencing high coal combustion temperatures; this indicates isotopically distinct phases in the fly ashes that react differently as leaching progressed.

Table 3 Strontium isotope ratio ($^{87}Sr/^{86}Sr$) of CUB column leachates. Vol (L) represents cumulative volume through the columns at the time of collection.

Date of sample collection-->		7/10/07		7/13/07		7/16/07		8/22/07		10/3/07	
Experiment	Vol. (L)	$^{87}Sr/^{86}Sr$ [a]	Vol. (L)	$^{87}Sr/^{86}Sr$ [a]	Vol. (L)	$^{87}Sr/^{86}Sr$ [a]	Vol. (L)	$^{87}Sr/^{86}Sr$ [a]	Vol. (L)	$^{87}Sr/^{86}Sr$ [a]
FA24										
Acetic Acid	0.23	0.711166 ±08	0.61	0.711159 ± 08	1.31	0.711083 ±07	9.84	0.711235 ± 10	19.35	0.711724 ± 11
Na Carbonate	0.26	na [b]	0.80	na [b]	1.16	na [b]	10.72	na [b]	21.93	na [b]
Nitric Acid	0.1	0.711005 ±12	0.77	0.711049 ± 09	1.44	0.711144 ± 08	11.07	0.712773 ± 11	21.22	0.713758 ± 08
FA38										
Acetic Acid	0.21	0.710757 ± 09	0.59	0.710746 ± 07	1.33	0.710753 ± 08	10.82	0.710751 ±11	20.99	0.710816 ±09
Na Carbonate	0.2	0.710758 ± 09	0.78	0.710744 ± 07	1.63	0.710760 ±09	11.67	na [b]	22.99	na [b]
Nitric Acid	0.16	0.710770 ± 08	0.69	0.710762 ± 08	1.38	0.710778 ± 11	11.40	0.711006 ± 10	22.67	0.711433 ±11
FA41										
Acetic Acid	0.23	0.712008 ±09	0.64	0.712019 ±09	1.15	0.712054 ±09	11.10	0.712051 ±12	22.29	0.712059 ±08
Na Carbonate	0.11	0.712022 ±10	0.91	0.711924 ±09	1.72	0.711929 ±09	11.59	na [b]	22.59	0.712111 ±11
Nitric Acid [b]	0.13	0.712008 ±10	0.64	0.712023 ±12	0.79	0.712031 ±06		clogged		clogged
FA49										
Acetic Acid	0.2	0.710967 ± 09	0.72	0.710850 ± 07	1.55	0.710817 ± 10	11.53	0.710934 ± 11	22.60	0.711021 ±11
Na Carbonate	0.25	0.710968 ± 11	0.83	0.710954 ± 06	1.69	na [b]	11.70	na [b]	23.03	na [b]
Nitric Acid	0.14	0.710946 ± 09	0.76	0.710833 ± 08	1.46	0.710864 ±09	11.71	0.711524 ±10	23.31	0.711828 ±12

na [b] = not analyzed due to high blank/sample ratio or insufficient sample size.

[a] = in run precision reported as 2σ error.

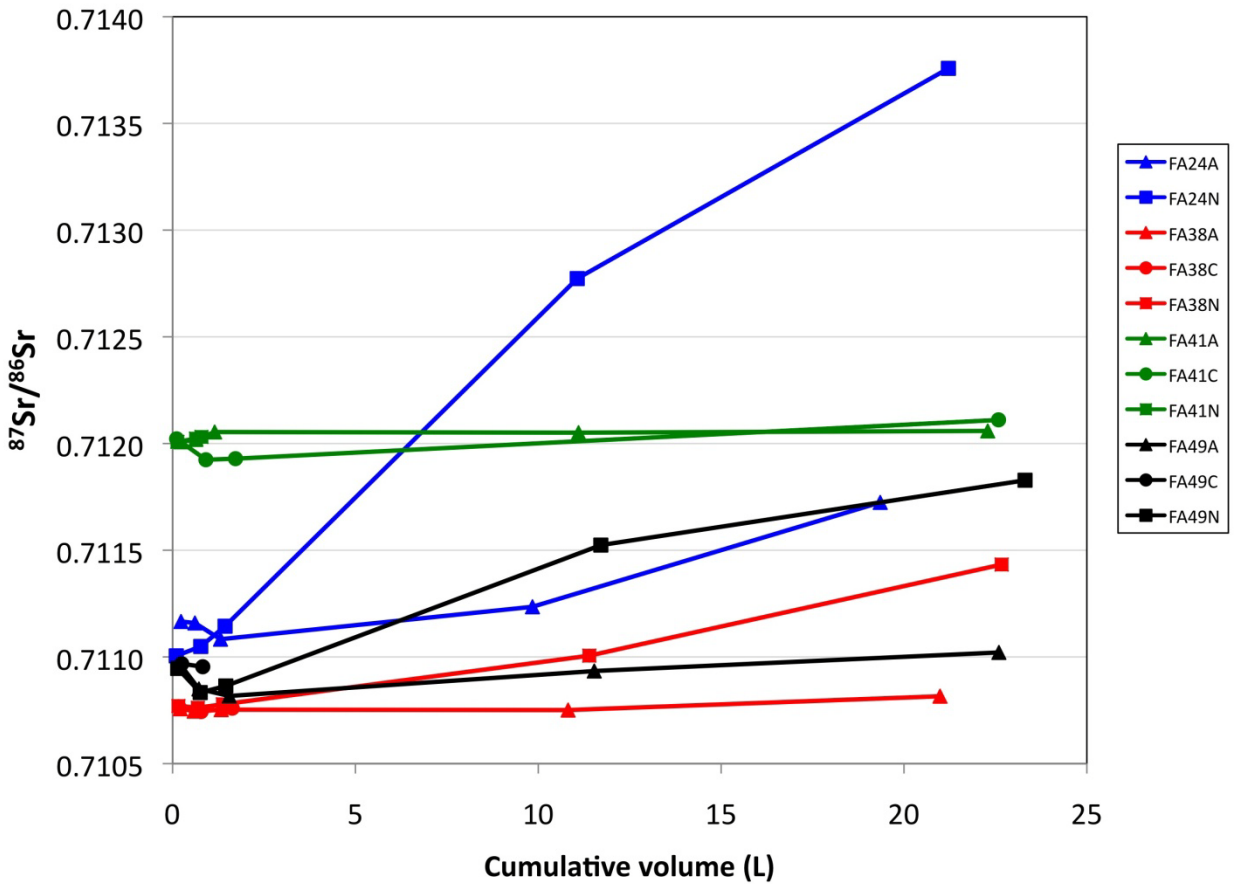

Figure 3 Variation in strontium isotope composition ($^{87}Sr/^{86}Sr$) of the leachate with cumulative volume leached in column experiments. Each fly ash sample is plotted as a different color, and A = acetic acid (triangles), N = nitric acid (squares) and C = sodium carbonate (circles).

4.3 BATCH LEACHING EXPERIMENT – ELEMENTAL AND SR ISOTOPIC DATA

Elemental concentrations of fly ashes FA24, FA24 duplicate, FA38 and FA49 are given in Table 4. Samples FA24 and FA24 duplicate showed good agreement in most major and minor element concentrations, indicating that the batch leaching procedure is reproducible. Concentrations of the same major elements reported for the column experiments are plotted in Figure 4. All of the fly ash samples exhibit increasing concentrations of K and Si as the batch leaching experiment progressed from Milli-Q water (MQW) to acetic acid (HOAc) to hydrochloric acid (HCl). The concentration of calcium did not follow a clear pattern; in sample FA24, maximum concentrations were encountered with the water leach, whereas samples FA38 and FA49 showed [Ca] maxima with the acetic acid leach. Maximum sulfur concentrations were encountered with the hydrochloric leach in FA24, while the highest amount of sulfur was removed with the water leach for FA38 and FA49.

Strontium isotope ratios for the batch leaching experiments are given in Table 5. Ratios for samples FA24 and FA24 Duplicate MQW and acetic acid leaches were not analyzed due to high blank/sample ratios or insufficient sample size. Sample $^{87}Sr/^{86}Sr$ ratios are plotted versus different batch leachates in Figure 5. Fly ash FA38 shows a gradual increase in $^{87}Sr/^{86}Sr$ ratio, with a starting ratio of 0.710743±09 in the water leach and a final $^{87}Sr/^{86}Sr$ ratio of 0.710846±10 in the hydrochloric acid leach. Sample FA49 exhibited a different pattern of strontium isotope ratio release with a ratio of 0.710876±07 in the water leach, followed by a ratio of 0.710798±10 in the acetic acid leach, increasing to a final ratio of 0.710958±09 in the hydrochloric leach. The HCl leachates for samples FA24 and FA24 duplicate plot at relatively high $^{87}Sr/^{86}Sr$ ratios of 0.711099±11 and 0.711107±10, respectively, and show excellent agreement in their strontium isotope ratios.

Table 4 Elemental data from sequential batch leaches with ultraclean water (MQW), acetic acid (HOAc) and hydrochloric acid (HCl). All concentrations reported as mg element leached per g CUB starting material.

Experiment	Al	B	Ba	Ca	Fe	K	Mg	Na	S	Si	Sr
FA24											
MQW	<DL	0.0251	0.000255	0.327	0.00172	0.0115	0.0435	0.0348	0.328	<DL	0.000403
HOAc	0.174	0.0124	0.0114	0.203	0.0157	0.0254	0.0245	0.00691	0.0245	0.0881	0.00302
HCl	0.807	0.0149	0.0574	0.269	0.256	0.250	0.0728	0.184	0.670	0.309	0.0269
FA24 Duplicate											
MQW	<DL	0.0235	0.000341	0.330	<DL	0.0113	0.0463	0.0325	0.333	<DL	0.000362
HOAc	0.175	0.0125	0.0141	0.167	0.0176	0.0244	0.0137	0.00336	0.00477	0.0888	0.00298
HCl	0.864	0.0151	0.0557	0.261	0.248	0.249	0.0750	0.176	0.624	0.277	0.0266
FA38											
MQW	0.260	0.332	0.00115	7.38	0.00235	0.00668	0.0226	0.227	3.46	0.468	0.0481
HOAc	0.427	0.247	0.00479	10.7	0.0105	0.0157	1.26	0.115	0.524	1.36	0.0541
HCl	4.83	0.180	0.120	6.58	3.11	0.385	0.725	0.361	1.21	5.21	0.145
FA49											
MQW	0.380	0.111	0.00563	5.47	0.00316	0.0808	0.0173	0.122	2.26	0.251	0.0428
HOAc	0.351	0.0493	0.0266	10.5	0.0270	0.0415	0.861	0.0397	0.232	0.810	0.0509
HCl	1.53	0.0466	0.0469	4.09	2.52	0.285	0.249	0.284	0.599	2.27	0.0522

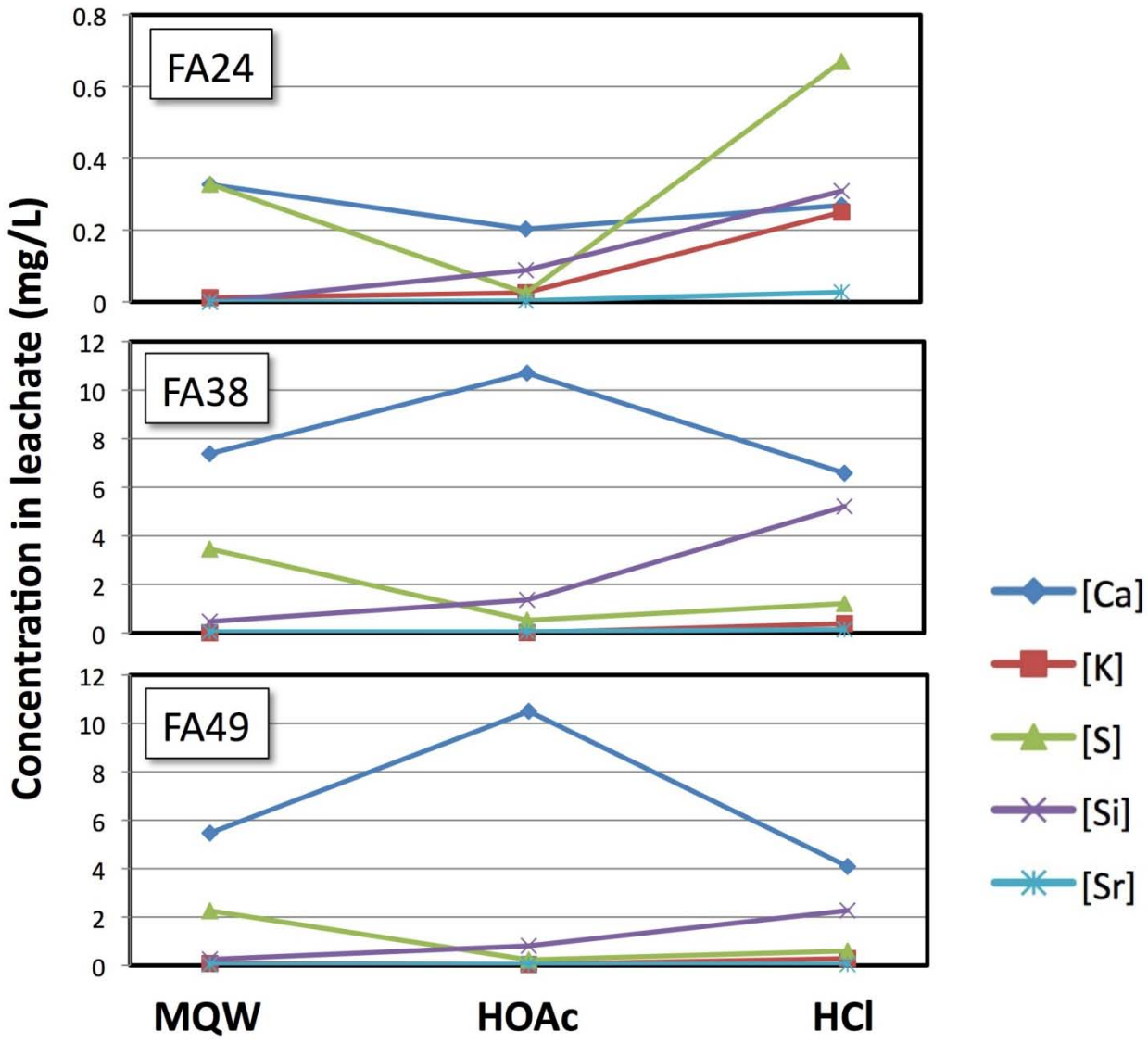

Figure 4 Major element concentrations of sequential batch leaches of fly ash.

Table 5 Strontium isotope composition (87Sr/86Sr) of fly ash sequential batch leachates. In-run precision reported as 2-sigma uncertainty.

Leachate	MQW	HOAc	HCl
FA24	na	na	0.711099 ±11
FA24 duplicate	na	na	0.711107 ±10
FA38	0.710743 ±09	0.710758 ±10	0.710846 ±10
FA49	0.710876 ±07	0.710798 ±10	0.710958 ±09

na = not analyzed due to high blank/sample ratio or insufficient sample size

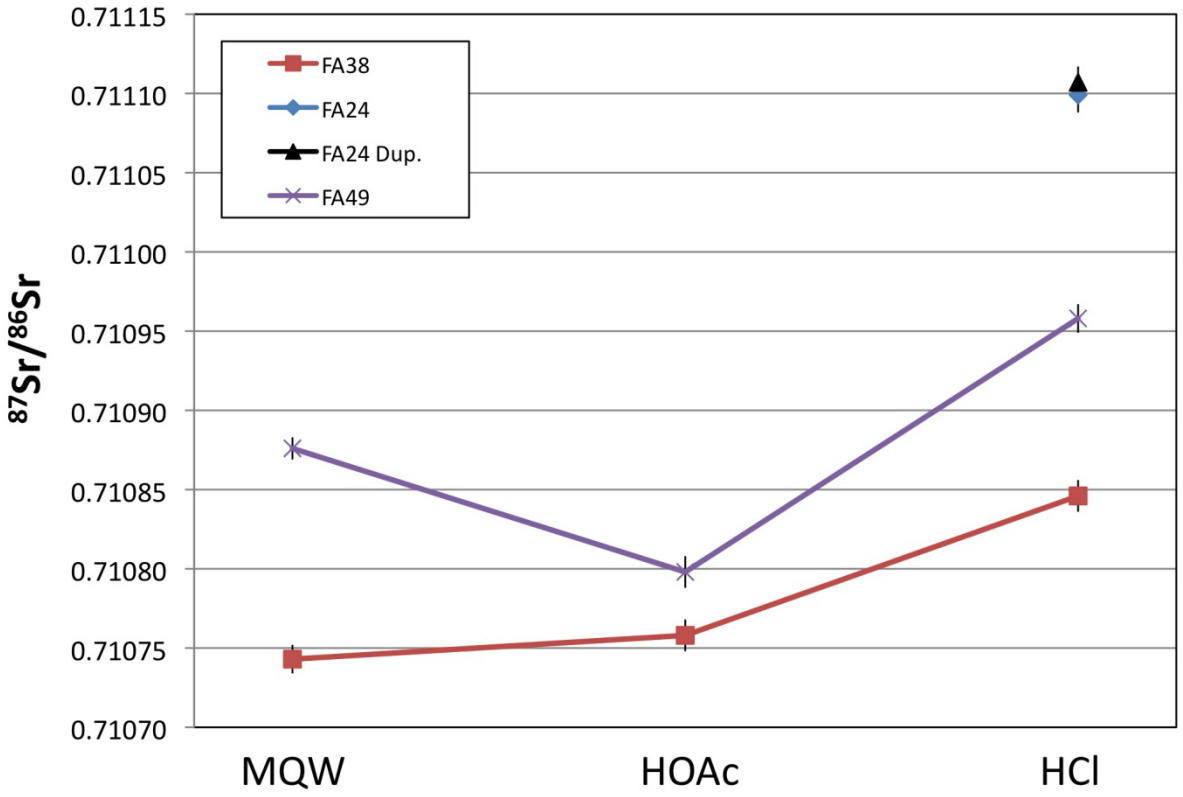

Figure 5 Strontium isotope variations in sequential batch leaches of fly ash.

5.0 DISCUSSION

5.1 COLUMN LEACHING EXPERIMENTS

Most of the leachate $^{87}Sr/^{86}Sr$ ratios fall within the range of values measured by Spivak-Birndorf (Spivak-Birndorf, 2007) on batch leachates of class F fly ash samples. The major exception is the last FA24 nitric acid leach ($^{87}Sr/^{86}Sr = 0.71376$), which falls well above the highest measured value in the previous study (0.71190).

The release of major elements during column leaching experiments in general follows a trend of high initial concentrations in the leachate, slowly diminishing with time (Fig. 2), with the exceptions of Si and Fe. The overall pattern of decreasing concentrations would be expected as surface-bound elements are released and soluble phases are dissolved, especially for base cations such as Ca, K and Sr. Sulfur is most likely to be held primarily as sulfate minerals, and these are likely to be solubilized early in the experiment, as observed. Calcium in FA24 shows a peak in mobilization near the middle of the acetic acid leaching experiment, which suggests that there is a slightly more resistant Ca-bearing phase such as a carbonate present in this fly ash. For the base cations, most ashes exhibit a release trend in which the greatest amount of element released correlates with the strength of the acid, i.e., HNO_3 > HOAc > Na_2CO_3 (base). Only sulfur is significantly removed by Na-carbonate in comparison to the other reagents, which

supports the suggestion that it is held in sulfate minerals such as anhydrite, found in some fly ashes and other CUB materials (Vassilev and Vassileva, 1996; Karayigit and Gayer, 2001).

Silica concentrations in all fly ash sample leachates except FA24 increase over time, likely indicating a gradual dissolution of a primary silicate mineral, a combustion-formed silicate phase, or combustion-formed glass. The increase in [Si] and [Fe] over time may reflect the removal of the buffering capacity of soluble minerals in the fly ash over the first few days of the experiments.

The strontium isotope system may provide additional information about the phases that are dissolved during the leaching of fly ash by environmental fluids. If the combustion process were to completely mix and isotopically homogenize strontium, then all phases leached during interaction with fluids would yield identical $^{87}Sr/^{86}Sr$ ratios. This is clearly not the case, as all samples showed significant variations in Sr isotope composition over the course of the experiments reported here. Another way to examine this is to look at the Sr isotopic composition as a function of the total amount of strontium extracted. In most cases, the experiments show a clear trend of increasing $^{87}Sr/^{86}Sr$ with increasing amount of extraction of Sr from the fly ash, as illustrated by sample FA38 (Fig. 6). This suggests that a residual silicate phase from the original coal mineral matter with a high $^{87}Sr/^{86}Sr$ ratio, such as biotite, muscovite or a clay mineral, has survived the coal combustion process without losing all of its strontium. This suggestion is backed by the correlation between $^{87}Sr/^{86}Sr$ and the [K]/[Sr] ratio (a proxy for the Rb/Sr ratio) seen in most samples (Fig. 7). In Figure 7, a less pronounced linear relationship between $^{87}Sr/^{86}Sr$ and [K]/[Sr] can be seen for sample FA41, as data for the nitric leach is unavailable due to a column clog. We can assume that if the nitric experiment for this sample were allowed to progress, eventually the high [K]/[Sr], more radiogenic phase would be accessed by the leachant

and a more linear relationship would be seen. If this late-dissolving phase were a glass formed during coal combustion, it would most likely inherit the isotopic composition of the bulk fly ash, which is likely to be much lower in most cases.

Previous mineralogical studies of CUB materials show that fly ash contains quartz and secondary quartz formed from silica liberated during phase transitions of clays, mica and feldspars, and also contain feldspars that may form during solid phase reactions between aluminosilicates and liberated Ca, K, and Na oxides (Vassilev and Vassileva, 1996; Kim and Kazonich, 2004). The more easily leachable phase within the fly ash could possibly be Ca and Mg oxyhydroxides that are a product of the decomposition of carbonate or are formed from organically and sulfate combined Ca and Mg (Vassilev and Vassileva, 1996), which would account for the higher proportions of Ca, Mg and S in the beginning stages of the experiment. It is also possible that some larger mineral particles may only be partially melted, due to shorter residence times in the high temperature zone or higher melting temperatures (Vejahati et al., 2010).

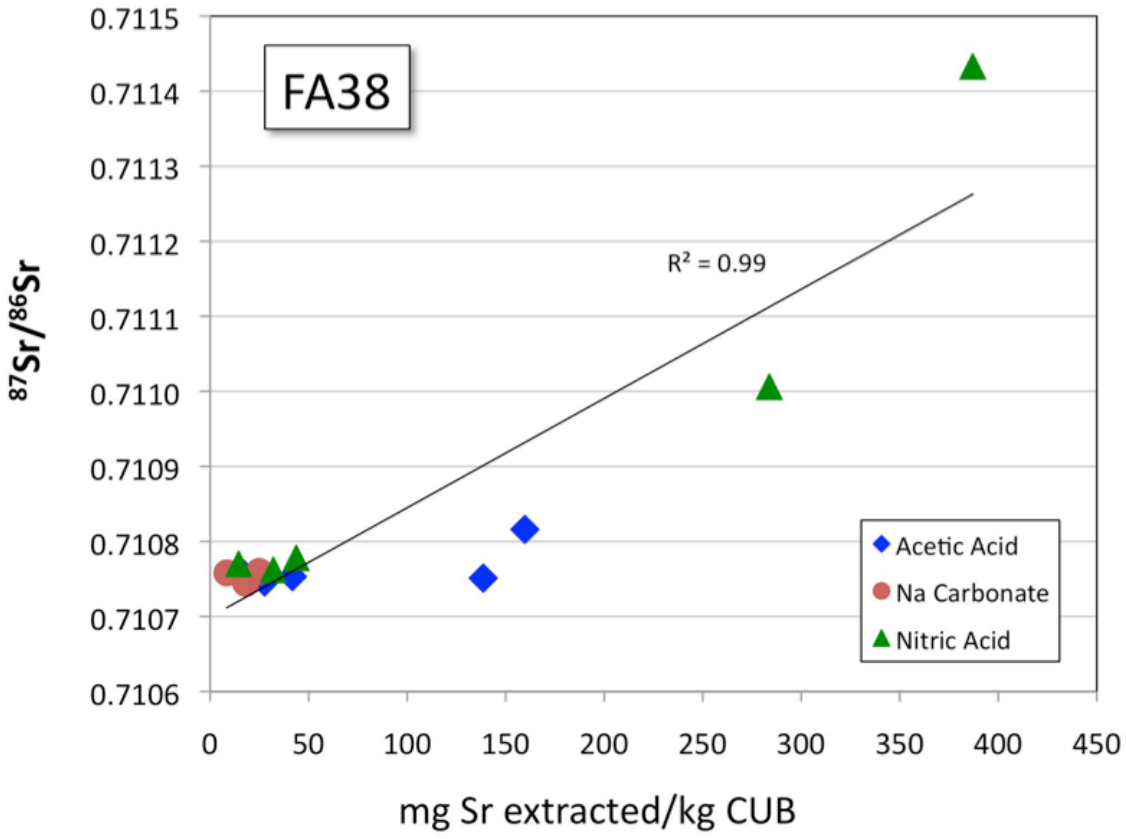

Figure 6 Strontium isotope variations ($^{87}Sr/^{86}Sr$) as a function of the amount of Sr extracted during the column leaching experiments on sample FA38. The data follow a general trend of increasing $^{87}Sr/^{86}Sr$ with increasing amount of Sr extracted.

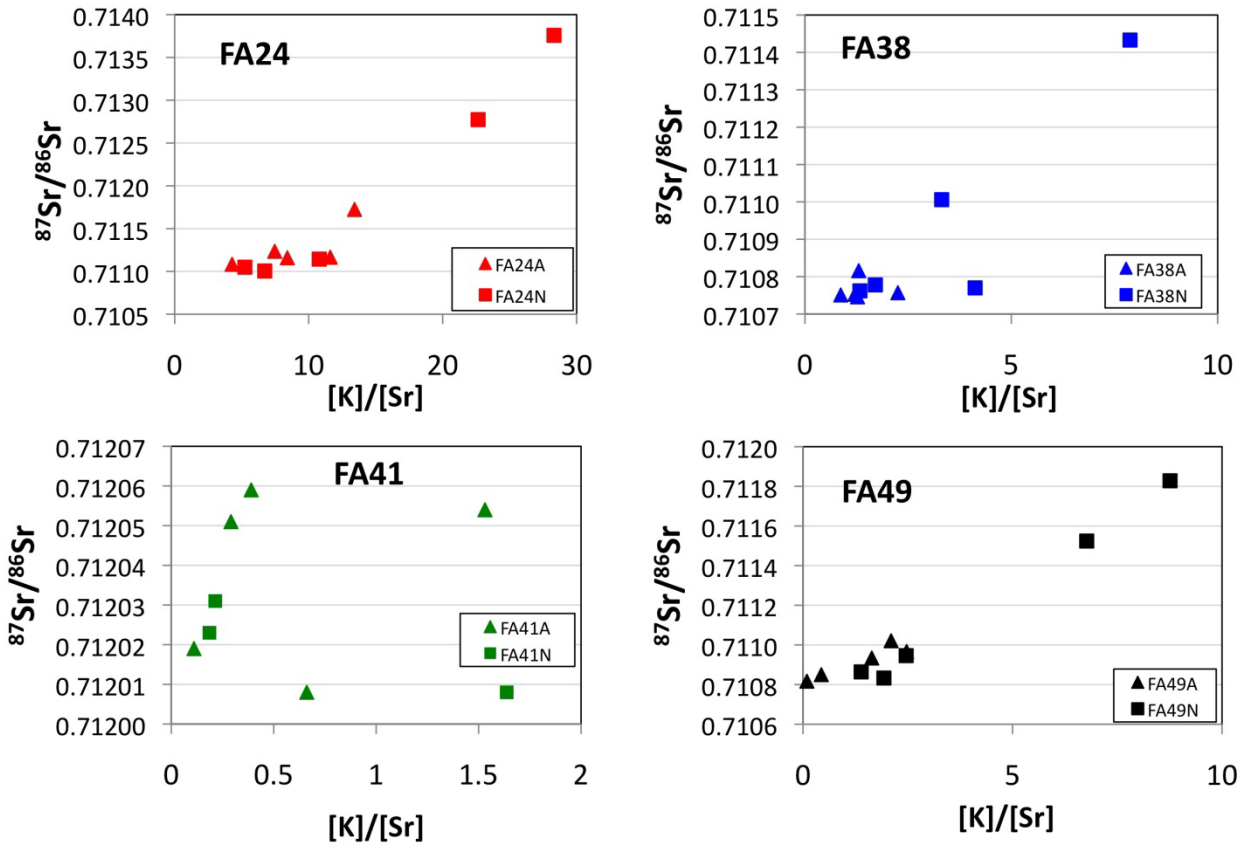

Figure 7 Strontium isotope variations ($^{87}Sr/^{86}Sr$) as a function of the K/Sr mass ratio in column leachates. In most cases there is a strong correlation between these variables.

5.2 BATCH LEACHING EXPERIMENTS

The presence of the same highly leachable fraction observed with the column experiments is supported by the low $^{87}Sr/^{86}Sr$ ratios seen in the H_2O and HOAc leachates. Strontium isotope ratios for the nitric acid leachates have the highest $^{87}Sr/^{86}Sr$ signatures for each respective fly ash, suggesting the presence of a radiogenic mineral phase that is more resistant to leaching. Figure 8 demonstrates the good correlation between the Sr isotopic ratio and the [K]/[Sr] ratio for the batch leachates.

Despite the different leaching techniques and different reagents used in the column and the batch leaching experiments, the results of this study show that the general trends are similar. The degree of extraction of most major elements correlates with the strength of the acid acting on the fly ash, with the exception of sulfur. The removal of soluble phases that are buffering the fly ash-fluid system then allows attack of more resistant minerals with higher $^{87}Sr/^{86}Sr$ ratios. The magnitude of this effect is similar in both the batch and column leaching experiments. Figure 9 shows that the batch and column leachate data follow the same general isotopic trend as strontium is extracted. Nitric acid is an oxidizing agent and hydrochloric acid is reducing; the results suggest that redox conditions are not as important a factor as the extent of CUB reaction.

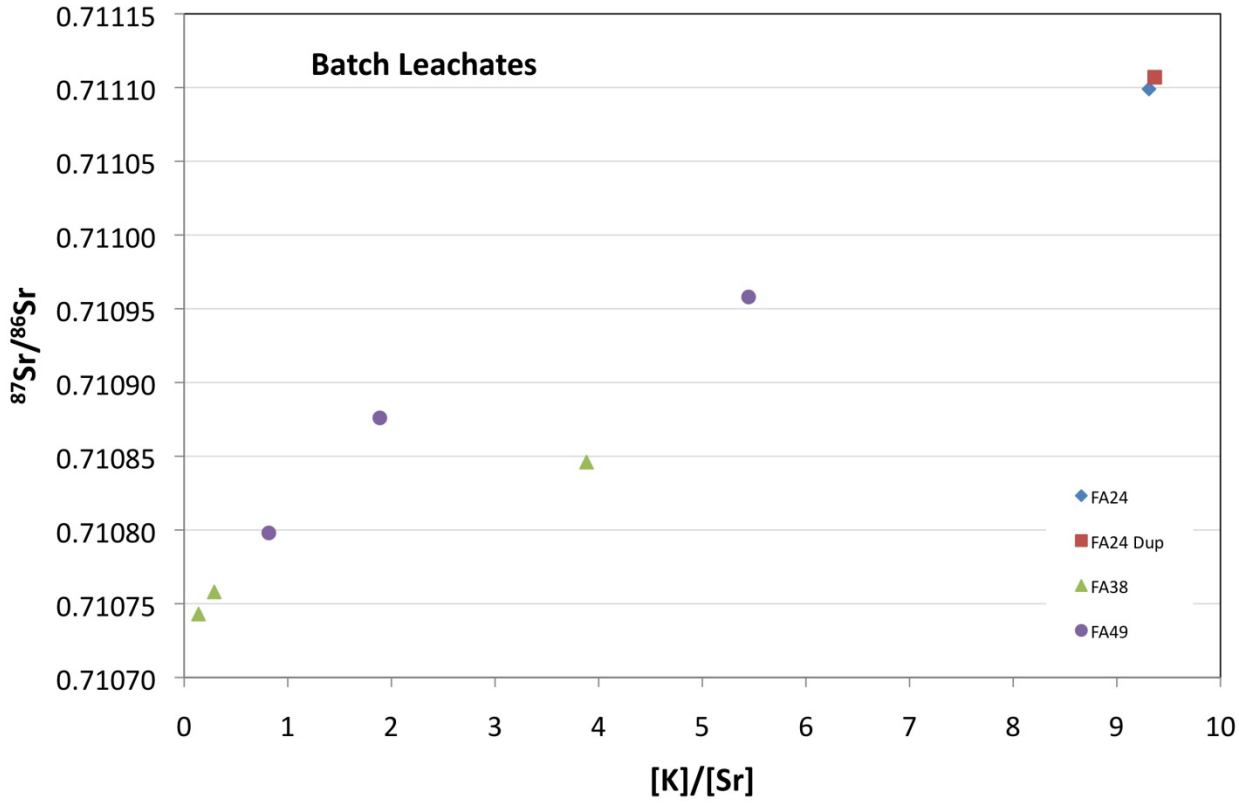

Figure 8 Strontium isotope variations ($^{87}Sr/^{86}Sr$) as a function of the K/Sr mass ratio in batch leachates.

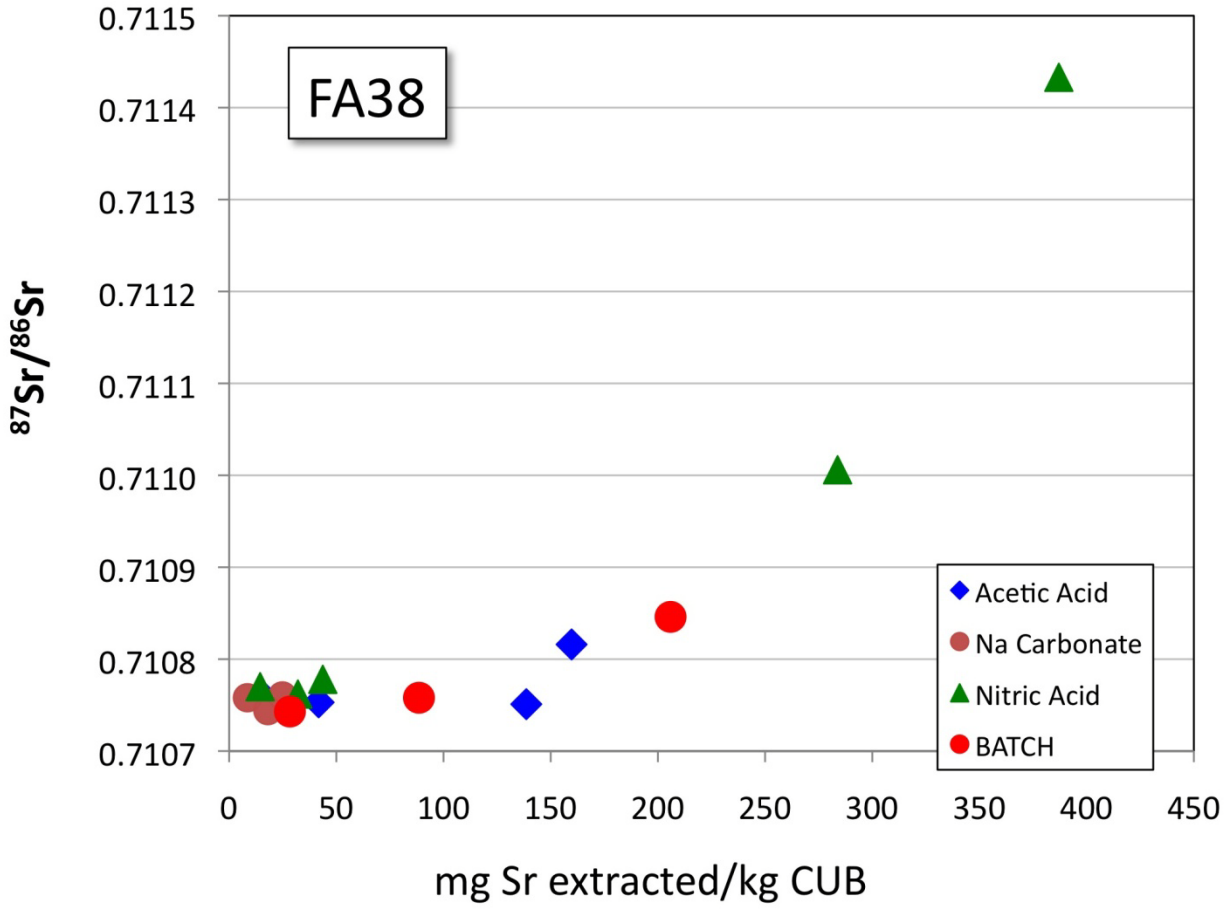

Figure 9 Strontium isotope variations ($^{87}Sr/^{86}Sr$) as a function of the amount of Sr extracted during the column leaching experiments on sample FA38 (as in Fig. 6), with the batch leaching data added (red circles). The batch leaching data fit in well with the column leaching data.

5.3 IMPLICATIONS FOR MONITORING FLY ASH LEACHING

Strontium isotopes have the potential to be used for identifying the interaction between fly ash and environmental fluids in areas of fly ash disposal or reuse. As shown here, the bulk of the strontium that is relatively soluble tends to have a narrow range of isotope compositions for a given fly ash; only after that Sr is removed does the $^{87}Sr/^{86}Sr$ ratio climb as the fluids attack residual silicate phases. Different batches of fly ash also tend to have significantly different $^{87}Sr/^{86}Sr$ ratios, which make it likely that Sr isotopes can be used as a forensic tool in field situations.

A key issue that this study highlights is the mineral association of elements released by leaching of fly ash. The high-$^{87}Sr/^{86}Sr$ residual phases, most likely glass or primary to secondary silicate minerals, could be reservoirs for elements of environmental concern, although this needs to be established through additional studies of the CUB residue. In a field situation, a changing $^{87}Sr/^{86}Sr$ ratio of leaching fluids could signal a shift in the minerals that are being attacked by the fluids, and thus indicate an impending shift in leachate chemistry. Additional detailed work on element-mineral-isotope associations is warranted.

6.0 CONCLUSIONS

This study presents an investigation of the strontium isotope systematics and geochemistry of coal utilization byproducts and their interactions with laboratory systems simulating environmental waters. Both column and batch leaching procedures were combined with Sr isotope analysis to identify distinct geochemical reservoirs within the CUB. Several samples of Class F CUB were analyzed to more fully understand the behavior of distinct phases within the CUB, as well as possible elemental associations and leaching patterns.

Analysis of elemental data from both the column and sequential leaching procedures shows an initial rapid release for most major elements, excluding silicon, suggesting association with soluble and surface bound phases. Possible sulfate mineral phases can be inferred due to the high proportions of S leached with sodium carbonate solution, effective at dissolving sulfates such as anhydrite ($CaSO_3$). In both the column and sequential leaching procedures silicon was leached most effectively by stronger acidic solutions later in the experiment, suggesting the presence of a more resistant silicate phase, possibly residual biotite, feldspar, or clays, or an amorphous glass phase formed during combustion.

The presence of distinct heterogeneous phases within CUB is also supported by isotopic data. Isotopic results from the column leaching experiment show a marked increase in $^{87}Sr/^{86}Sr$ ratio with continued leaching. This general trend is also seen in the sequential leaching data, showing an increase in $^{87}Sr/^{86}Sr$ ratio with continued leaching in increasingly acidic solutions.

These data show that there are isotopically distinct phases within the CUB, suggesting the presence of a more resistant, highly radiogenic phase that survives the combustion process and is leached after the more soluble minerals are removed. The Sr isotope systematics and leaching behavior of the Class F CUB samples demonstrate that isotopic homogenization of minerals in coal does not always occur during the combustion process, despite the high temperatures encountered in the boiler.

Column flow-through and sequential batch extraction leaching techniques yield similar patterns of element removal, and both show the same pattern of Sr isotope evolution with increasing Sr extraction. Different CUB samples tend to yield distinct $^{87}Sr/^{86}Sr$ values which persist at a relatively constant level while the easily extractable Sr is removed, then begin to rise with increasing exposure to the leachate. This suggests that the key factor in accessing more resistant phases within CUB appears to be the extent of leaching, rather than the particular leaching procedure or acid used.

The individual samples of CUB analyzed in this study have distinct Sr isotopic compositions, suggesting that Sr would potentially be a sensitive tracer for the interaction of CUB with environmental fluids. The presence of isotopically distinct reservoirs with varying elemental associations and solubility in CUB is of concern, as potentially toxic metals and trace elements may be leached from these materials when stored in ponds, used as soil amendments, or used for remediation of acid mine drainage.

BIBLIOGRAPHY

ACAA, 2004. 2003 Coal Combustion Product (CCP) Production and Use Survey, Aurora, CO.

Asokan, P., Saxena, M. and Asolekar, S.R., 2005. Coal combustion residues—environmental implications and recycling potentials. Resour. Conserv. Recycl., 43: 239-262.

Banner, J.L., 2004. Radiogenic isotopes: systematics and applications to earth surface processes and chemical stratigraphy. Earth-Sci. Rev., 65: 141-194.

Bhattacharyya, S., Donahoe, R.J. and Patel, D., 2009. Experimental study of chemical treatment of coal fly ash to reduce the mobility of priority trace elements. Fuel, 88: 1173-1184.

Bignoli, G., 1989. Health and environmental impact of chromium released from coal ash. Journal of Coal Quality, 8: 72-81.

Capo, R.C., Stewart, B.W. and Chadwick, O.A., 1998. Strontium isotopes as tracers of ecosystem processes: Theory and methods. Geoderma, 82: 197-225.

Depoi, F.S., Pozebon, D. and Kalkreuth, W.D., 2008. Chemical characterization of feed coals and combustion-by-products from Brazilian power plants. Int. J. Coal Geol., 76: 227-236.

Dutta, B.K., Khanra, S. and Mallick, D., 2009. Leaching of elements from coal fly ash: Assessment of its potential for use in filling abandoned coal mines. Fuel, 88: 1314-1323.

Feeley, T.J., III., Murphy, J., Brickett, L.A. and Aljoe, W.W., 2004. A Review of DOE/NETL's Coal Utilization By-Products Environmental Characterization Research.

Hamel, B.L., Stewart, B.W. and Kim, A.G., 2010. Tracing the interaction of acid mine drainage with coal utilization byproducts in a grouted mine: Strontium isotope study of the inactive Omega Coal Mine, West Virginia (USA). App. Geochem., 25: 212-223.

Hassett, D.J., 1998. Synthetic groundwater leaching procedure. In: R.A. Meyers (Editor), Encyclopedia of Environmental Analysis and Remediation. John Wiley & Sons, Inc., Hoboken, NJ, pp. 4797-4803.

Hassett, D.J., Pflughoeft-Hassett, D.F. and Heebink, L.V., 2005. Leaching of CCBs: observations from over 25 years of research. Fuel, 84: 1378-1383.

Hurst, R.W. and Davis, T.E., 1981. Strontium isotopes as tracers of airborne fly ash from coal-fired power plants. Env. Geol., 3: 363-367.

Hurst, R.W., Davis, T.E. and Elseewi, A.A., 1991. Strontium isotopes as tracers of coal combustion residue in the environment. Env. Geol., 30: 59-77.

Karayigit, A.I. and Gayer, R.A., 2001. Characterization of fly ash from the Kangal Power Plant, eastern Turkey, International Ash Utilization Symposium, Center for Applied Energy Research, University of Kentucky, pp. 1-8.

Kim, A.G., 2003. Leaching methods applied to CUB: Standard, regulatory and other, 15th International Symposium on Management and Use of Coal Combustion Products, St. Petersburg, FL, pp. 29-1-29-12.

Kim, A.G. and Hesbach, P., 2009. Comparison of fly ash leaching methods. Fuel, 88: 926-937.

Kim, A.G. and Kazonich, G., 2004. The silicate/non-silicate distribution of metals in fly ash and its effect on solubility. Fuel, 83: 2285-2292.

Kutchko, B.G. and Kim, A.G., 2006. Fly ash characterization by SEM-EDS. Fuel, 85: 2537-2544.

Mackowsky, M.-T., 1982. The application of coal petrography in technical processes. In: E.D. Stach et al. (Editors), Stach's Textbook of Coal Petrology. Gebrüder Borntraeger, pp. 413-474.

Martinez-Tarazona, M.R., Spears, D.A., 1996. The fate of trace elements and bulk minerals in pulverized coal combustion in a power station. Fuel Process. Technol., 47: 79-92.

Querol, X., Fernández-Turiel, J.L. and López-Soler, A., 1995. Trace elements in coal and their behaviour during combustion in a large power station. Fuel, 74: 331-343.

Querol, X. et al., 2001. Extraction of soluble major and trace elements from fly ash in open and closed leaching systems. Fuel, 80: 801-813.

Ruhl, L. et al., 2009. Survey of the potential environmental and health impacts in the immediate aftermath of the coal ash spill in Kingston, Tennessee. Env. Sci. Technol., 43: 6326-6333.

Shukla, K.N. and Mishra, L.C., 1986. Effect of fly ash extract on growth and development of corn and soyabean seedling. Water Air Soil Poll., 27: 155-167.

Spivak-Birndorf, L., 2007. Strontium isotope systematics and geochemistry of coal utilization by-products. Masters Thesis, University of Pittsburgh, Pittsburgh, 56 pp.

Straughan, I.R. et al., 1981. Fly ash-derived strontium as an index to monitor deposition from coal-fired power plants. Science, 212: 1267-1269.

Vassilev, S.V. and Vassileva, C.G., 1996. Mineralogy of combustion wastes from coal-fired power stations. Fuel Process. Technol., 47: 261-280.

Vejahati, F., Xu, Z. and Gupta, R., 2010. Trace elements in coal: Associations with coal and minerals and their behavior during coal utilization – A review. Fuel, 89: 904-911.

Xu, M., Yan, R. and Zheng, C., 2004. Status of trace element emission in a coal combustion process: a review. Fuel Process. Technol., 85: 215-237.

Yeheyis, M.B., Shang, J.Q. and Yanful, E.K., 2008. Characterization and environmental evaluation of Atikokan coal fly ash for environmental applications. J. Environ. Eng. Sci., 7: 481-498.

Ziemkiewicz, P.F., Simmons, J.S. and Knox, A.S., 2003. The mine water leaching procedure: Evaluating the environmental risk of backfilling mines with coal ash. In: K.S. Sajwan, A.K. Alva and R.F. Keefer (Editors), Chemistry of Trace Elements in Fly Ash. Kluwer Academic/Plenum Publishers, New York, pp. 75-90.